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FREEZE-SPRAY PROCESSING OF LAYERED CERAMIC COMPOSITES (PREPRINT)

O. Jongprateep, Q. Fu, A. Abbott, and F. Dogan

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14. ABSTRACT
Thermal gradients and associated stresses are critical in designing with ceramic composites having low thermal conductivity. In order to reduce the stresses from thermal gradients, compositional gradients are employed in designing of composite structures. This study addresses development of freeze-spray process to fabricate layered ceramic structures with controlled layer thickness and microstructural development. The composites were processed by spraying of ceramic slurries with low binder content and relatively high solids loadings (up to 40 vol%) on a cooled substrate. The frozen parts were freeze-dried and sintered at elevated temperatures. The relationship between microstructural development and thermal expansion behavior of Al_2O_3 and Y_2O_3-stabilized ZrO_2 functionally graded ceramic composites is discussed.

15. SUBJECT TERMS
freeze spray, rapid prototyping, ceramic composites, thermal gradients

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Introduction

Functionally graded materials are a new generation of engineered materials that have become of much interest in recent years. The graded materials are ideal candidates for various applications ranging from functional and structural materials. Such applications involve severe thermal gradients, such as components in advanced aerospace engines, and thermal barrier coatings for tools, to biomedical implants.[1-2] A gradual transition of material compositions in a solid creates gradual variations in microstructural development which may lead to an enhancement of material properties.[3-4]

The present study describes the development of a freeze-spray process for rapid fabrication of graded lamina composites. Freeze-spray process involves the preparation of ceramic slurries with a low binder content that are sprayed onto a cold substrate to obtain a compositional gradient. Frozen parts are then subjected to freeze drying process, so that green bodies with low binder content can be obtained.[5-6] The process is also suitable when spray-freezing of non-aqueous slurries are required[7,8]. Since the green bodies contain relatively low amounts of binder, a rapid binder burn-out process can be employed for large volume parts prior to the sintering. Freeze-spray process is a versatile and relatively simple technique to fabricate graded structures of various materials which may not be obtained by other methods such as lamination of green tapes processed by tape casting or thermal (plasma) spray processes.

By changing slurry compositions during freeze-spray process, one can achieve gradual compositional changes between dissimilar materials in layered composite structures. Such materials may find various applications particularly in high temperature

environments where strong temperature gradients exist and require reduced internal stresses in graded composites. In this study, alumina-zirconia graded laminar composites are fabricated to demonstrate the feasibility of freeze-spray process followed by freeze-drying.

Experimental procedure

Alumina (A16SG: Alcoa, USA) and 5.3 weight% (3 mol%) yttria-stabilized zirconia (Sigma Aldrich, USA) powders were used for preparation of slurries. The average particle sizes of powders were d_{50}: 0.40 μm for alumina and d_{50}: 0.82 μm for zirconia. Alumina and zirconia aqueous slurries with a solids loading of 30-50 volume% were prepared using 1.2 wt% ammonium polymethacrylate (Darvan C: Vanderbilt, USA) and 3 wt% acrylic emulsion polymer (Duramax: Rohm and Haas, USA). The amount of organic additives in weight percentage was calculated based on the weight of the powders. The optimum dispersant amount for slurries was determined by particle settling experiments. Well dispersed slurries were obtained by ball milling for 48 hours in polypropylene bottles. Viscosity of the slurries was measured using a rotating concentric cylinder viscometer (Haake, Model VT500) with shear rates at 0–500 s^{-1}.

The samples consisting of alumina and zirconia layers were obtained by spraying of slurries on a cooled substrate. The thickness of each layer was controlled by repetitive spraying of slurries on frozen material. Figure 1 shows a computerized 3D-gantry system equipped with a spray nozzle (Iwata, Model HP-BCS) used to spray thin layers of slurries on a cryogenically cooled metallic plate. The slurries freeze almost instantly, forming solid structures. The experimental set-up could be enclosed in a cooled chamber and dry

atmosphere as needed. Frozen samples were freeze-dried under vacuum at -20°C to remove the ice by sublimation. In order to study the effect of green density on the sintered microstructure, a set of samples were isostatically pressed at a pressure of 250MPa. After freeze-drying, the samples underwent a binder burn-out process at 550°C with a heating rate 1°C/min. Sintering of the samples was carried out at 1550°C for 6 hours with a heating and cooling rate 5°C/min.

The sintering density of the samples was measured by Archimedes method. Thermal expansion behavior of sintered materials was investigated using a dilatometer (Orton, Model 1600). Coefficient of thermal expansion (CTE) of materials was determined from the linear change in the length of the samples as a function of temperature. Microstructural and elemental analyses were conducted on the polished and fracture surfaces of the samples using a scanning electron microscope, SEM (JEOL, Model T330), and an energy dispersive x-ray spectrometer, EDS (Hitachi, Model S-4700 FESEM).

Results and discussion

Freeze-spray process of graded materials requires a delicate control of slurry properties and spray conditions. To achieve dense ceramic structures after sintering, the slurries should have high solids loadings yet still have a low enough viscosity to be dispensable without causing clogging of the nozzle. Preparation of well dispersed and stable slurries is essential to prevent flocculation of the particles in the liquid which in turn affects the uniformity of the layer during deposition process and microstructural

development of green and sintered bodies. Electrostatic, steric and electrosteric stabilization are common techniques employed in preparation of stable slurries.[9-11]

Ammonium polymethacrylate was used as a dispersant to achieve steric stabilization in the slurries. Alumina and zirconia slurries with solids loadings of 30, 35, 40, 45 and 50 vol% were prepared and characterized by viscosity measurements. Fig. 2 shows that all slurries exhibit shear thinning behavior. It is revealed that the increase of viscosity as a function of solids loading is more pronounced for zirconia slurries as compared to that for alumina slurries. Note that at high shear rates, the shear stress of the zirconia slurry with 50 vol% solids loading was too high for the sensor to be measured and not included in Fig. 2. Viscosities of alumina and zirconia slurries with 30 and 45vol% are compared separately in Fig. 3. While at low solids loadings (30 vol%) no significant difference between the viscosities of both slurries was observed, viscosities of zirconia slurries were higher than that of alumina slurries at higher solids loadings (45 vol%).

Dispensing behavior of the slurries with the spray nozzle used in this study is strongly affected by the slurry viscosity which depends on the level of solids loading. Slurries with solids loadings up to 30 and 40 vol% could be sprayed uniformly without clogging of the spray nozzle. However, at higher solids loadings, slurries became highly viscous and were more difficult to spray continuously. As the solids loading of the slurries increased to 45 vol% and higher, clogging of spray nozzle was experienced, particularly for zirconia slurries. Based on the observations made from viscosity measurements and dispensing behavior of slurries, the optimum range of the solids loading was 35 to 40 vol% so that uniform spray pattern could be obtained without clogging of spray nozzle.

The sintering density of alumina samples, fabricated using slurries with 35vol% solids loading, ranged from 75 to 86 % of theoretical density. To obtain higher densities, green samples were isostatically pressed at 250MPa. Isostatic compaction of freeze-dried alumina samples resulted in 90-98 % theoretical density after sintering. The microstructural development of sintered alumina prepared with and without isostatic compaction of freeze-dried samples is shown in Fig. 4. It is evident that unpressed samples are highly porous while denser microstructures are obtained after isostatic compaction. Higher green and sintering densities could be obtained by spraying of slurries with higher solids loading and lower viscosity which could be prepared using organic additives[5].

Laminar alumina and zirconia composites were processed by freeze-spray deposition of alternating layers as shown in Fig. 5. The EDS analysis of the samples revealed that the layers of dark contrast are alumina while the layers of bright contrast correspond to zirconia. Relatively pore-free alumina/zirconia interface is revealed. To obtain unique designs for microstructural development, laminated structures with smooth, wavy or more complex shape interfaces can be processed by adjusting the spray conditions during slurry deposition. Fig. 5 reveals that the thicknesses of alumina and zirconia layers are in the range of 200-300μm and 80-100μm, respectively. During deposition process, alumina and zirconia slurries were sprayed for 10 passes to constitute each observed layer. Each pass for spraying of slurries corresponds to formation of alumina and zirconia layers with a thickness of 20-30μm and 8-10μm, respectively. The layer thickness can be adjusted by controlling the solids loading of slurries, the flow rate and the speed of nozzle movement during spray process.

Fig. 6 shows the microstructure of a graded structure composed of alumina, alumina/zirconia composite, and zirconia layers. Layers A, B, and C correspond to alumina, alumina/zirconia (1:1 volume ratio, buffer layer), and zirconia, respectively. Such structures could be utilized in high temperature applications to reduce internal stress development within the material when composites are exposed to extreme temperature gradients at elevated temperatures[12, 13]. As revealed in Fig 10, the interfaces between each layer are crack-free and appear to have a strong interfacial bonding. This can be attributed to alumina/zirconia buffer layer which forms a continuous alumina and zirconia at each interface.

Fig 7 shows that differential densification of alumina and zirconia layers during the sintering process may lead to warping of samples. Since densification of zirconia layer takes place at lower sintering temperatures as compared to that of alumina, excessive differential shrinkage due to constrained sintering may also result in crack formation perpendicular to the layers. The presence of a buffer layer can reduce the differential shrinkage so that less warping and crack-free samples can be obtained as shown in Fig 6. For the samples with planar geometries, the dimensional changes due to warping could be reduced by controlling of porosity of each layer in green samples or by applying pressure during the sintering process.

To study the role of buffer composition on the bonding strength of interfaces, alumina and zirconia bilayers with and without a buffer layer were prepared. It is known that macroscopic defects at the interfaces can cause de-lamination and result in catastrophic failure of the composites[12]. While the interface between zirconia and alumina layers in Fig 8 shows formation of voids or microcracking, the interfaces

between alumina/buffer and zirconia/buffer layers are dense and free of micro-cracks (Fig. 9) as discussed previously. This indicates that the stress concentrations along the interface of alumina and zirconia layers caused by the mismatch of thermal expansion coefficients can be reduced by the presence of a buffer layer. Moreover, the composition within the buffer layer can be graded by changing the ratio of alumina/zirconia in the composite to achieve a graded transition between alumina and zirconia layers. Similarly, the thickness of the graded buffer layers can be optimized to meet the design requirements for structural components.

Figure 10 shows the microstructure of composites with decreasing ratio of alumina to zirconia which can be used as buffer layers for graded structures. Polished surfaces of the samples reveal a uniform distribution of alumina and zirconia grains within the composite. The fracture surface of the samples show equiaxed grains of the composites with an average grain size about 1μm. Graded buffer layers prepared using such compositions may prove to be beneficial for further reduction of internal stresses caused by high temperature gradients.

Measurement of the coefficient of thermal expansion (CTE) for alumina/zirconia composites are shown in Fig 11. The mean coefficient of thermal expansion was calculated using data collected between 250°C and 750°C. CTE values for alumina and zirconia were determined as 8.8×10^{-6}/°C and 11.3×10^{-6}/°C, respectively. It is revealed that the CTE increases linearly as the volume fraction (ranging from 0.2 to 0.8) of zirconia in alumina increases. Stress concentration at the interfaces caused by the mismatch of CTE between dissimilar materials can be reduced by the presence of a buffer layer which is composed of graded alumina/zirconia composites.

Summary

A freeze-spray deposition technique coupled with freeze-drying process was developed for rapid prototyping of alumina/zirconia lamellar structures. Such components may find various applications particularly in high temperature environments where a wide range of temperature gradients is present and a reduction of internal stresses in composite materials is required.

The process involves preparation of alumina and zirconia slurries with a solids loading in the range of 35-40vol% which were sprayed on a cooled substrate layer by layer to build desired structures. Rapid solidification of slurries with low binder content allows a rapid processing of composite materials. Freeze-dried parts were sintered and characterized by measurement of thermal expansion coefficients and studying of microstructural development. To achieve higher sintering densities, a set of freeze-dried samples were isostatically pressed.

Alumina and zirconia bilayers were processed with and without a buffer layer which was prepared using composite powders of alumina and zirconia. A graded interface between alumina and zirconia laminates using a buffer layer, was effective to reduce stress concentrations so that crack-free interfaces with strong bonding could be obtained. Linear dimensional change of the samples as a function of the temperature was determined by dilatometer measurements. The results were discussed with respect to microstructural development of graded ceramic composites.

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Figure captions

Figure 1 A preliminary experimental apparatus showing freeze-spray deposition technique for processing of layered structures.

Figure 2 Viscosity of alumina and zirconia slurries as a function of shear rate showing the effect of the solid loading on viscosity.

Figure 3 Comparison of viscosities of alumina and zirconia slurries with solids loadings 30 and 45 vol%.

Figure 4 Microstructural development of sintered alumina samples: a) as freeze-dried, b)freeze-dried and isostatically pressed.

Figure 5 SEM micrographs of alumina/zirconia layered structures processed by freeze-spray deposition.

Figure 6 SEM micrographs showing a cross sectional view of a) polished and b) unpolished alumina/buffer (50 vol% alumina + 50 vol% zirconia)/zirconia layered structures.

Figure 7 Image of an alumina/zirconia (left) and an alumina/buffer/zirconia (right) layered structures.

Figure 8 SEM micrographs showing micro cracks and voids along the alumina and zirconia interface

Figure 9 Microstructural development at the interface of alumina-zirconia buffer/alumina (left), and buffer/zirconia layers.

Figure 10 SEM micrographs of buffer layers a) 80% alumina + 20% zirconia, b) 60% alumina + 40% zirconia, and c) 20% alumina + 80% zirconia. Polished surfaces (left) and fracture surfaces (right). Note that the bright phase corresponds to zirconia.

Figure 11 Coefficient of thermal expansion (CTE) of alumina/zirconia composites as a function of zirconia volume fraction in alumina.

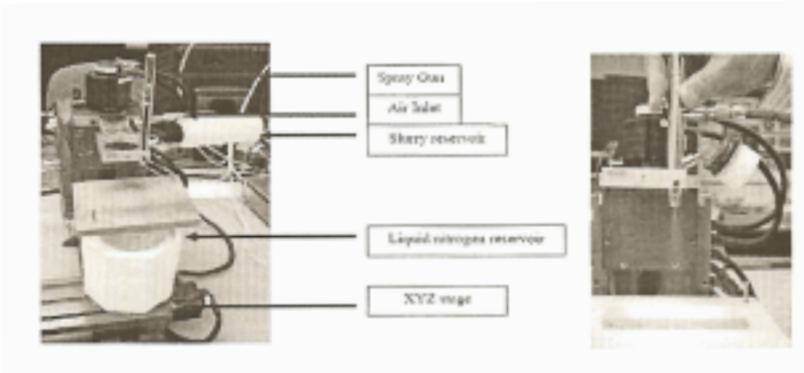
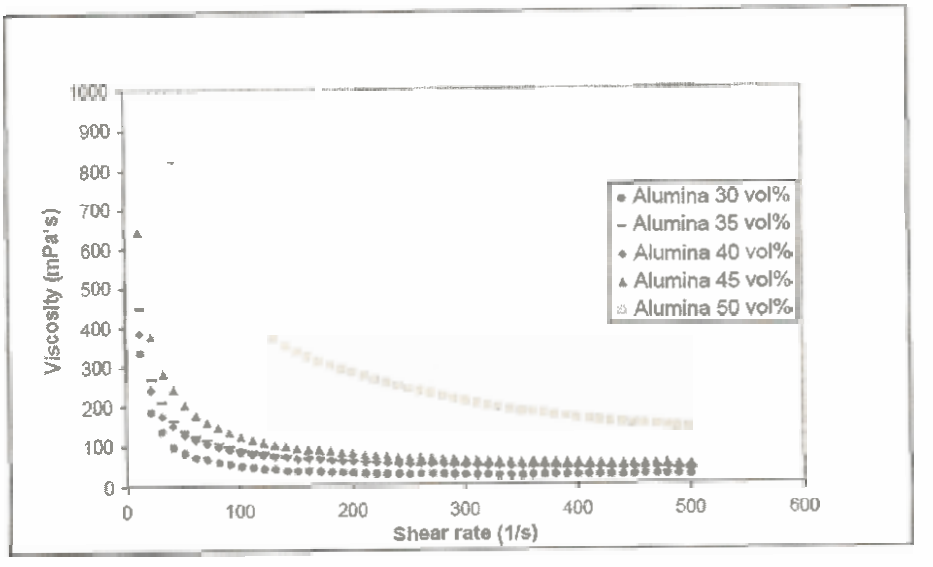

Spray Gun
Air Inlet
Slurry reservoir
Liquid nitrogen reservoir
XYZ stage

Figure 1.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Shear rate (1/s)
Alumina 30 vol%
Alumina 35 vol%
Alumina 40 vol%
Alumina 45 vol%
Alumina 50 vol%

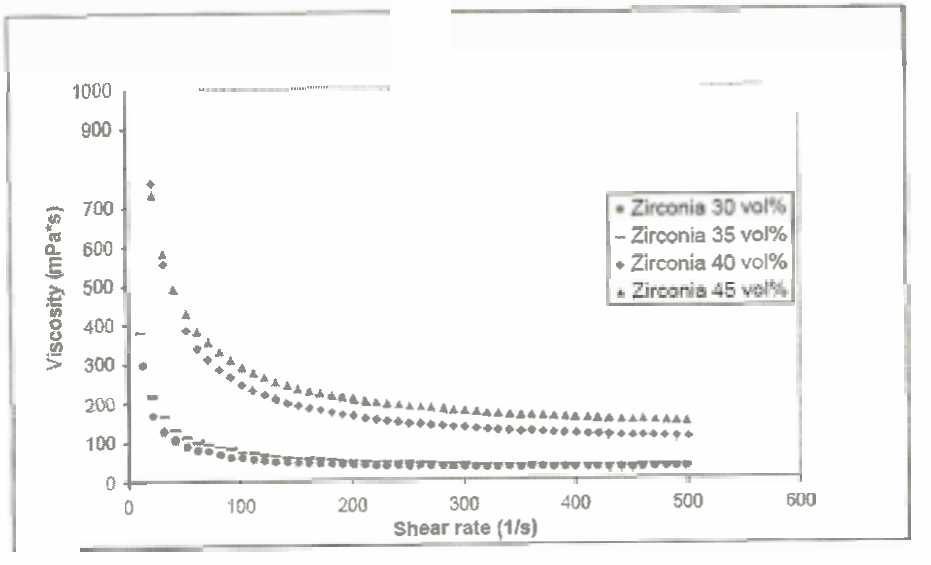

Viscosity (mPa*s)
Shear rate (1/s)
Zirconia 30 vol%
Zirconia 35 vol%
Zirconia 40 vol%
Zirconia 45 vol%

Figure 2

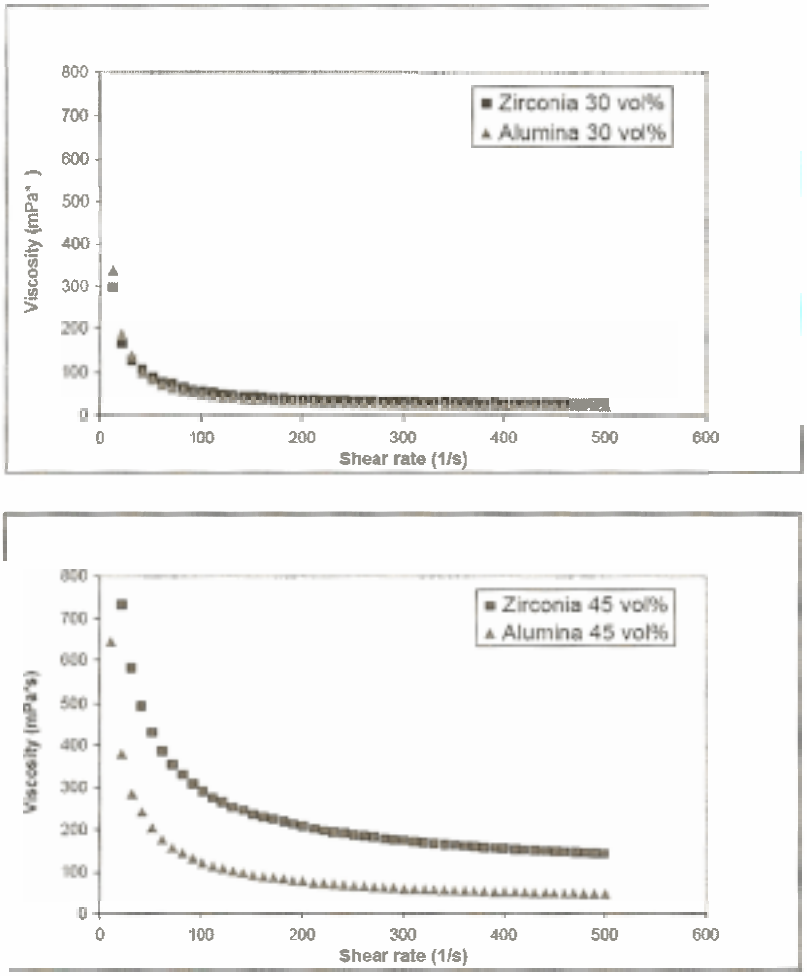
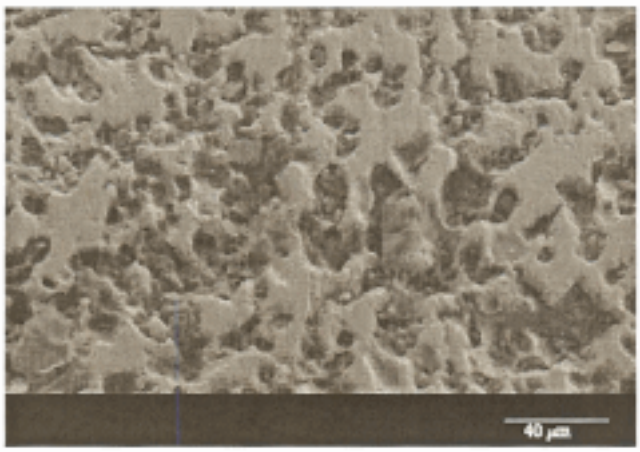

Zirconia 30 vol%
Alumina 30 vol%
Viscosity (mPa*s)
Shear rate (1/s)
0
100
200
300
400
500
600
700
800
Zirconia 45 vol%
Alumina 45 vol%
Viscosity (mPa*s)
Shear rate (1/s)

Figure 3.



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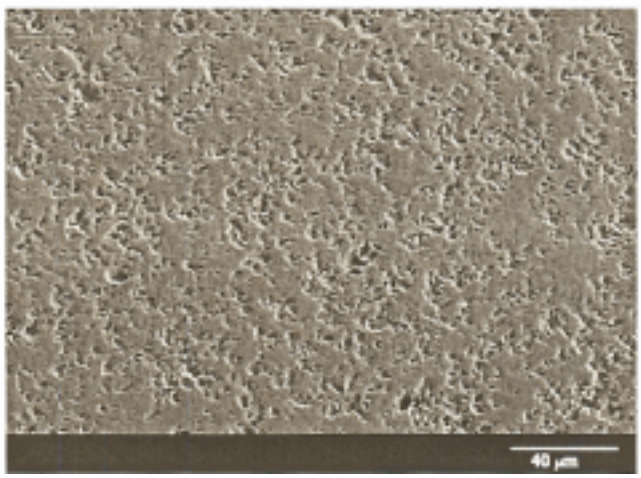

b)

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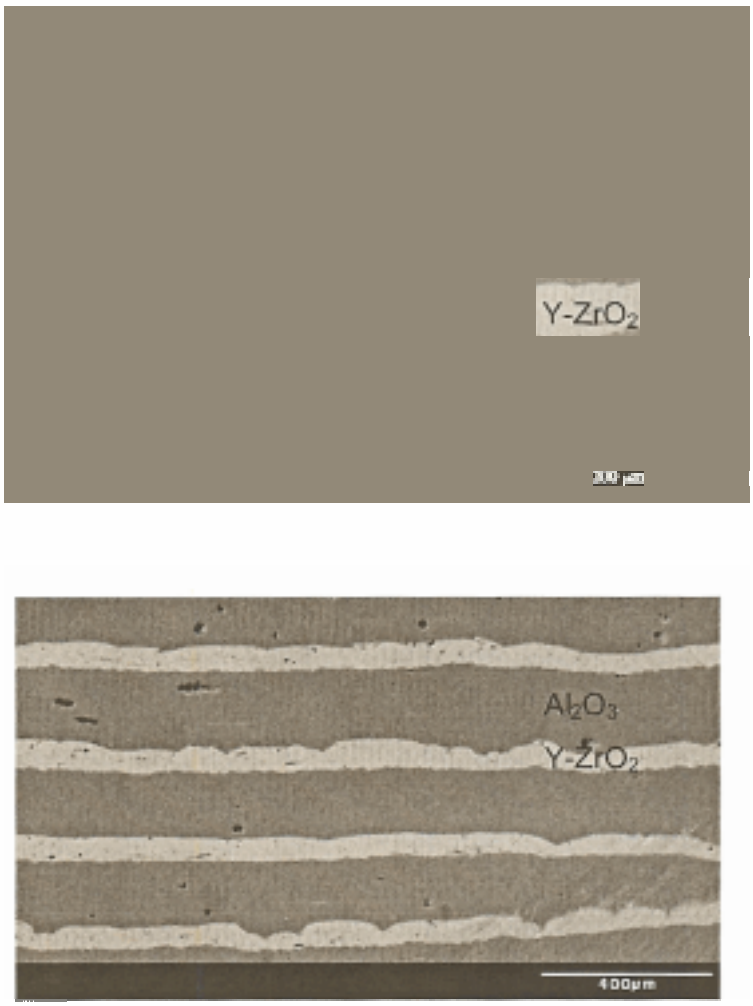

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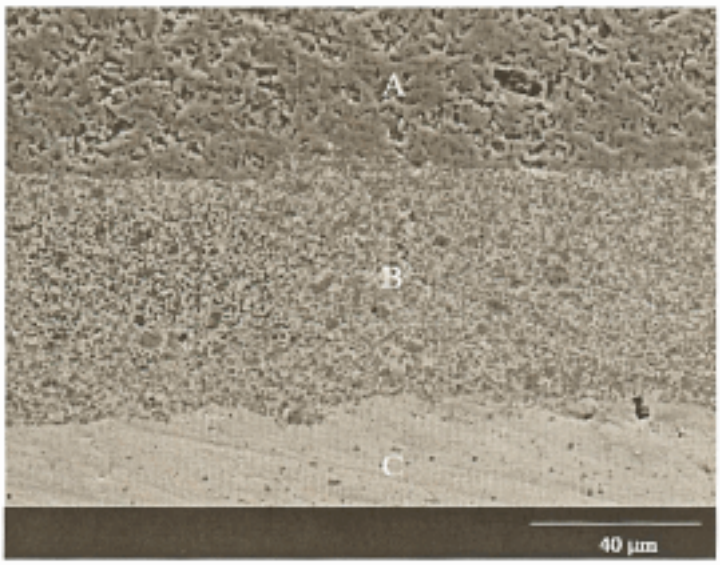

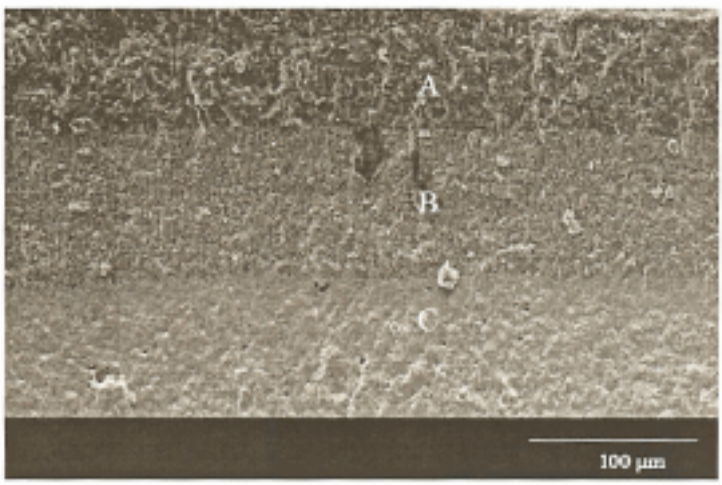

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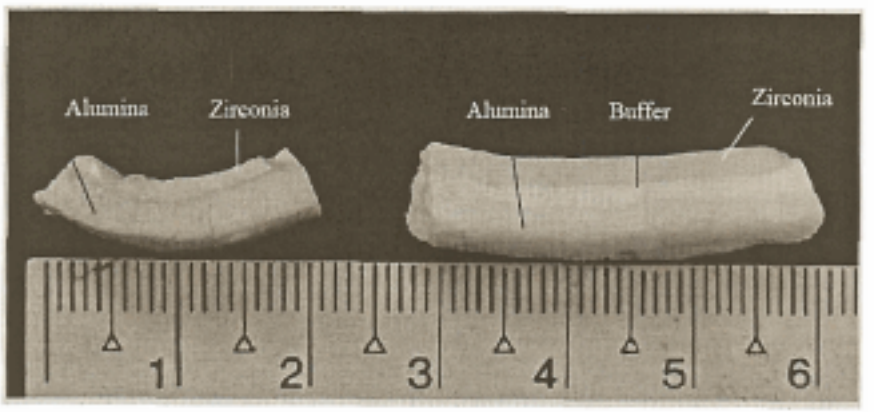

Figure 7.

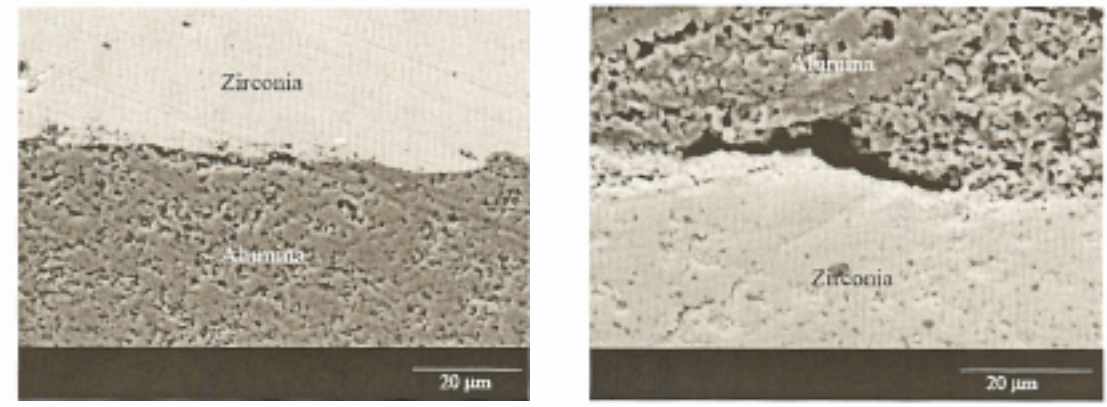

Figure 8

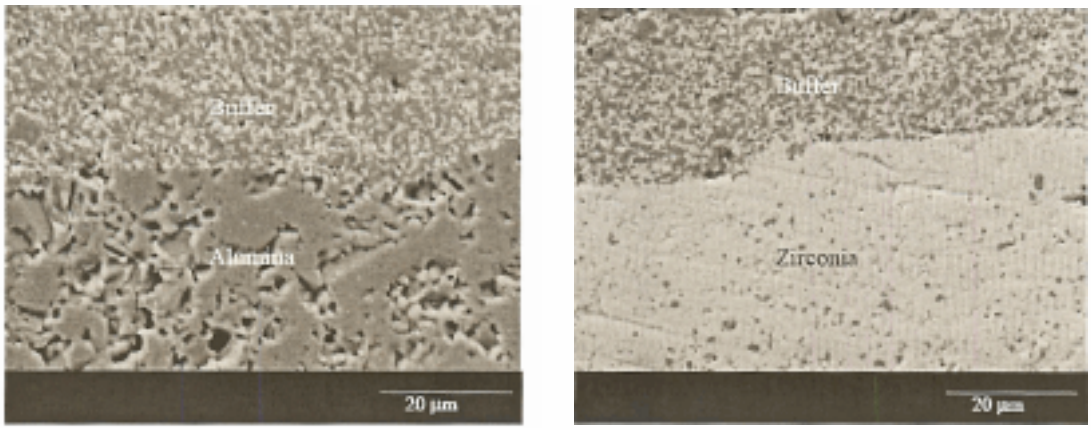

Figure 9

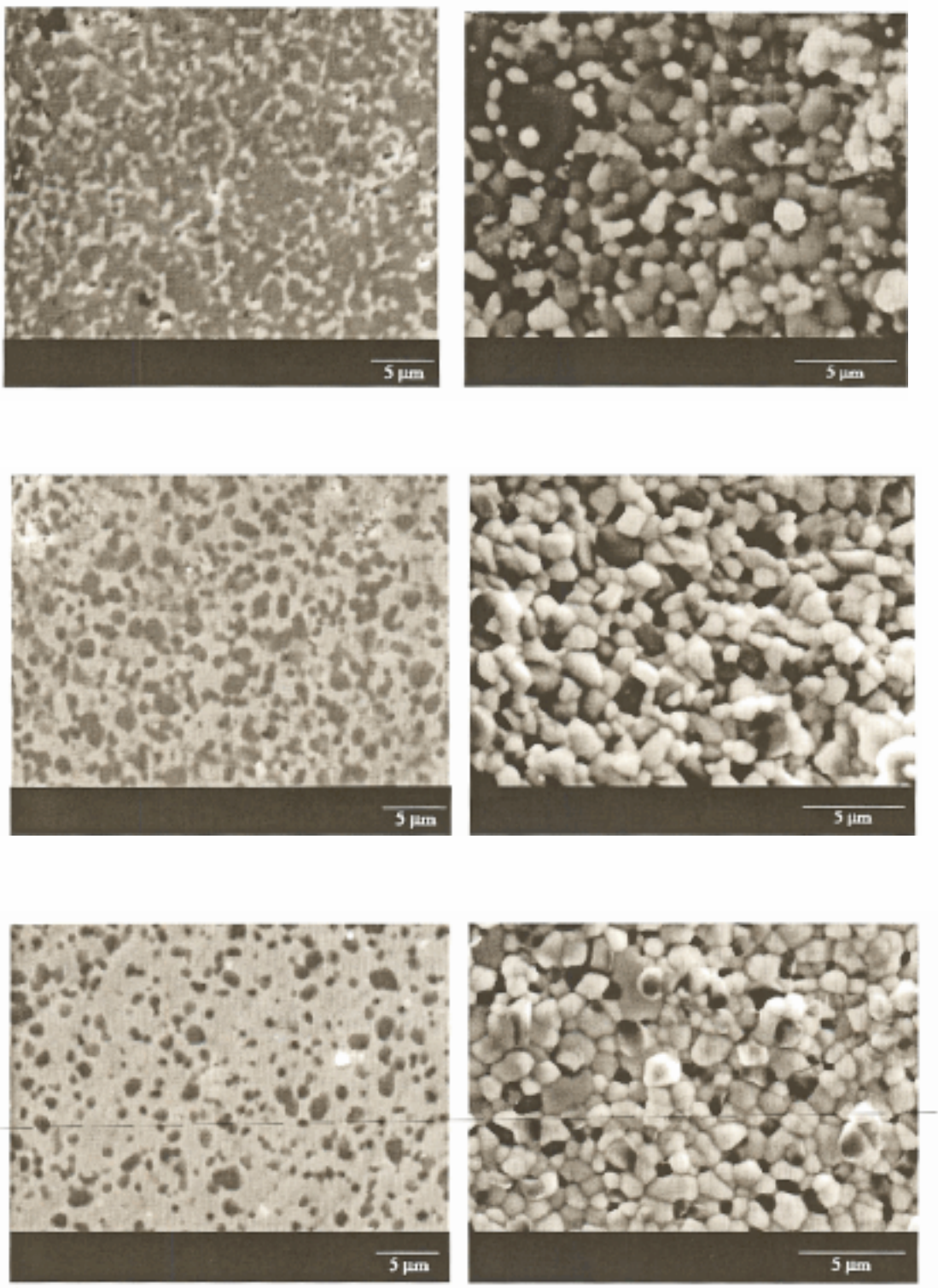

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Figure 10

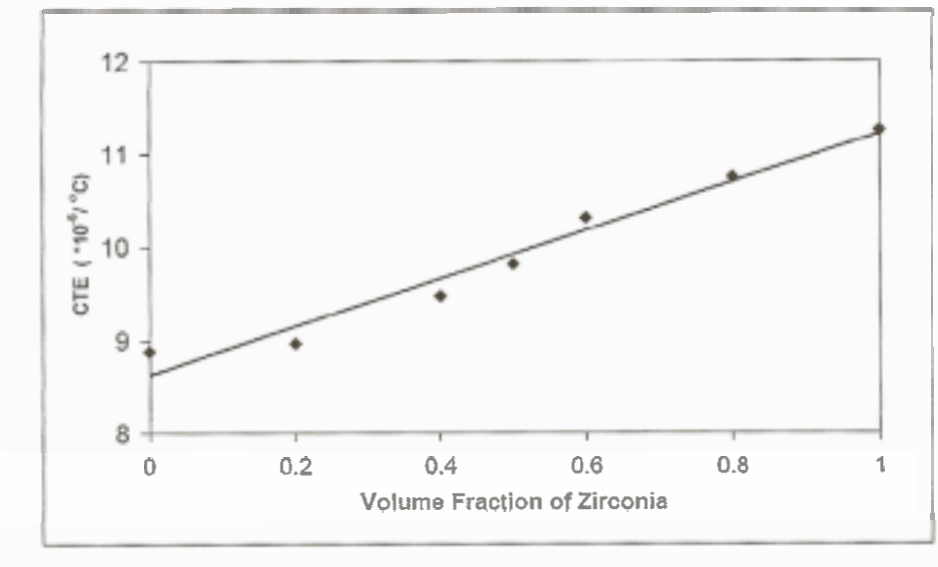

Figure 11.